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THE DETERMINATION OF OXIDES OF NITROGEN

BY

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THE DETERMINATION OF OXIDES OF NITROGEN.

By A. C. Allison, W. L. Parker, and G. W. Jones.

INTRODUCTION.

The Bureau of Mines in the course of its work for more efficient utilization of the mineral resources of the United States and the minimizing of accidents in the production of these mineral resources has occasion to make analyses of gases.

Gas analysis is an important part of the work in determining the ventilation conditions and the hazards that may develop from exposure of the workers to gases liberated in mines. Not only is it important to identify such gases as form explosive mixtures, and are at times liberated in large quantities, but in addition it is necessary to determine what gases have harmful effects upon miners who are exposed to them while at work. This paper offers what is believed to be an efficient method of determining the oxides of nitrogen.

At the time this paper was written an article by C. Toombs, entitled "Determination of nitrous fumes in mine air," appeared in the Journal of the South African Association of Analytical Chemists for 1919, volume 2, page 3, and was abstracted in volume 38 of the Journal of the Society of the Chemical Industry, page 267A. The same abstract appeared in Chemical Abstracts, volume 13 (Nov. 10, 1919), page 2650. It is possible that this paper may duplicate the work of Toombs, but the authors have been unable to obtain his original article for comparison.

ACKNOWLEDGMENTS.

The method of testing mine-air samples was suggested by A. C. Fieldner, supervising chemist of the Pittsburgh experiment station. Daniel Harrington, mining engineer of the Bureau of Mines, cooperated by sending a number of mine-air samples for testing the method as developed by the authors.

PRODUCTION OF OXIDES OF NITROGEN AND CARBON MONOXIDE.

In metal mines where much blasting is done, the shots are often prepared improperly, and some oxides of nitrogen may be formed after firing. Moreover, other industries than mining produce oxides

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of nitrogen which have a deleterious effect on individuals breathing them for any length of time.

Two gases that result from the firing of explosives are, because of their physiological effects, important in mine ventilation. They are carbon monoxide and oxides of nitrogen. Other gases produced at the same time, including carbon dioxide, hydrogen, methane, and nitrogen, are unimportant unless in proportions sufficient to diminish appreciably the oxygen content of the mine air. Carbon monoxide and oxides of nitrogen usually occur together and are very harmful even when inhaled in small quantities. About 0.01 or 0.02 per cent is the maximum quantity of carbon monoxide allowable continuously in mine air without affecting the workmen harmfully, although as much as 0.04 per cent is harmless for periods of time not exceeding one hour. Very little data are available on the maximum quantity of oxides of nitrogen that may be tolerated in mine air without danger to the men working therein. The general conclusions are that 0.01 or 0.02 per cent of oxides of nitrogen is dangerous and under no conditions should 0.05 per cent be reached. Carbon monoxide can be determined to an accuracy of about 0.02 per cent by the usual Haldane analysis, but an accurate method of determining oxides of nitrogen at low concentrations has heretofore been impossible without using a large quantity of gas for a sample.

HISTORICAL DATA.

A method was desired by which very small quantities of oxides of nitrogen could be determined from a minimum quantity of gas, for samples of mine gases are taken most conveniently in vacuum bottles of about 250-c. c. capacity; it is difficult to ship larger samples for great distances without the containers being broken.

The nitron method used by Gutbier[1] and Busch[2] is difficult to perform and can not be used at such low concentrations as are present in the usual mine-air samples. To be of value in mine-gas analysis, a method should be accurate to at least 10 parts per million, or 0.001 per cent. After explosives have been fired, especially in ventilated working faces, the products of the explosion are, of course, diluted with large quantities of air and the amounts of oxides of nitrogen present will usually be lower than 100 parts per million (0.01 per cent). To determine these small quantities, a method was adapted from the usual procedure for the determination of the oxides of nitrogen in water analysis,[3] applying the di-phenyl sulphonic acid method. The oxides resulting from the firing of explosive powders are chiefly nitric oxide and nitrogen peroxide. Nitric oxide is almost completely oxidized, in the presence of oxygen, to nitrogen peroxide, which in turn forms nitrous and nitric acids in the presence of water vapor. In consequence of the above facts, nothing is gained by determining the nitric and nitrous oxides separately, since the values found do not indicate the relative percentages present at the time when the explosive was fired and when the samples were taken. The method was therefore applied to give the total oxides of nitrogen as nitrogen peroxide or as nitrates. Nitrous oxide is completely oxidized to the peroxide[4] when treated with hydrogen peroxide and sodium hydroxide and boiled on a hot plate. The nitrates formed are subsequently determined by the usual water-analysis procedure as modified to apply to gases.

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[1] Gutbier, A., Die gewichtsanalytische Bestimmung der Salpetersäure mittels "Nitron" nach M. Busch: Ztschr. angew. Chem., Jahrg. 18, i, 1905, pp. 494–499.

[2] Busch, Max, Oxydation der salpetrigen Säure durch Wasserstoffsuperoxyd; Bestimmung von Nitrat neben Nitrit: Ber. Deut. chem. Gesell., Jahrg. 39, Bd. 2, 1906, pp. 1401–1403.

This colorimetric method was tested out with concentrations of sodium nitrate corresponding to those that would be obtained after oxidizing small quantities of oxides of nitrogen with sodium hydroxide and hydrogen peroxide.[5, 6]

The oxidizing reagents used did not affect the color reaction after provision had been made for neutralizing the excess alkali. Ten parts of oxides of nitrogen as nitrate could be detected in one million parts of the air oxides of nitrogen mixture with an accuracy of five or six parts per million.

REAGENTS.

Phenol-disulphonic acid.—Dissolve 25 grams of pure white phenol in 150 c. c. of concentrated sulphuric acid, add 75 c. c. of fuming sulphuric acid (15 per cent SO_3), stir well, and heat for two hours at 100° C.

Standard nitrate solution.—A solution of potassium nitrate is made containing 0.72 gram of KNO_3 per liter. Ten c. c. of this solution is evaporated on the water bath until about one drop is left and the remaining water is removed with a current of dry air. The residue is quickly and thoroughly moistened with 2 c. c. of the phenol-disulphonic acid solution and made up to one liter. One c. c. of this solution equals 0.001 mg. N_2.

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[3] Standard methods of water analysis: American Public Health Assoc., 3d ed., New York, 1917, p. 23.

[4] Tatlock, R. R., and Thomson, R. T., The analysis of waters and their changes in composition when employed in steam-raising: Jour. Soc. Chem. Ind., vol. 23, 1904, pp. 428–431.

[5] Chamot, E. M., Pratt, D. S., and Redfield, H. W., Study on the phenolsulfonic acid method for the determination of nitrates in water—The chief sources of error in the method: Jour. Am. Chem. Soc., vol. 33, 1911, pp. 366–381.

[6] Tatlock, R. R., and Thomson, R. T., The analysis of waters and their changes in composition when employed in steam-raising: Jour. Soc. Chem. Ind., vol. 23, 1904, pp. 428–431.

Other reagents include dilute NH_4OH (equal parts of strong NH_4OH and distilled water), 10 per cent NaOH solution, hydrogen peroxide, and a mixture of 50 parts of the phenol disulphonic acid and 50 parts of concentrated sulphuric acid.

PREPARATION OF THE STANDARDS.

The required amount of the standard nitrate solution is measured into a Nessler tube, 5 c. c. of the 1 to 1 NH_4OH added, and the whole made up to 100 c. c. with distilled water. The standards may be used for two to three weeks before a new batch needs to be made up.

In the calculation of the column marked "NO_2" in the table below, the gas laws are assumed to be obeyed.

TABLE 1.—*Standards used in determining oxides of nitrogen.*

Standard No.	Standard nitrate solution.	Value of standard.			Parts per million, based on 250 c. c. sample.
		MgN_2.	$MgNO_2$.	NO_2.	
	c. c.	*c. c.*	*c. c.*	*c. c.*	
1.	0	0.000	0.0000	0.00000	0
2.	1	.001	.0033	.00175	7
3.	2	.002	.0066	.00350	14
4.	4	.004	.0132	.00700	28
5.	7	.007	.0231	.01225	49
6.	10	.010	.0330	.01755	70
7.	15	.015	.0495	.02625	105
8.	20	.020	.0660	.03550	140
9.	25	.025	.0825	.04375	175
10.	30	.030	.0990	.05250	210
11.	35	.035	.1155	.06125	245
12.	40	.040	.1320	.07000	280

PROCEDURE.

A vacuum tube used for sampling mine air is shown in figure 1. Each tube is evacuated before it is sent to the mine where the samples are to be taken. A file mark is made on one side of the capillary neck and a sample of gas is taken by exerting pressure at this mark, thus breaking the tip. Gas immediately enters the capillary opening, filling the tube. Then the tube is sealed by forcing prepared wax into the opening, and is mailed to the Pittsburgh laboratory of the Bureau of Mines for analysis.

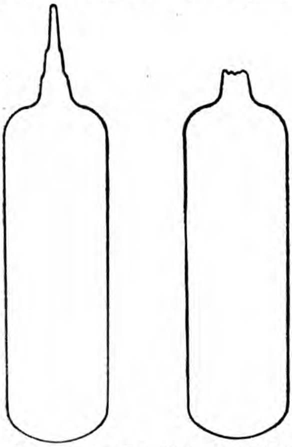
FIGURE 1.—Vacuum tube for sampling mine air.

When the sample is received at the laboratory, a file mark is made on the neck of the bottle below the capillary opening and the tube is broken at this point under mercury in a bell jar. The usual analysis is made for carbon dioxide, oxygen, carbon monoxide, hydrogen, and methane. Then the bottle is raised or lowered in the bell jar until the mercury both inside and outside is at the same level and the bottle is marked at this point. The tube is lifted from the jar, allowing the mercury to run out and air to enter. Next 5 c. c. of the 10 per cent NaOH solution and 5 c. c. of hydrogen peroxide are added and the opening is closed with a rubber stopper. The sample tube is rotated to coat the inside of the tube with a thin film of the oxidizing solution, and left for 30 minutes. The tube is then opened and washed through a filter paper into a 150 c. c. beaker and evaporated.

A very good method of evaporation (suggested by Dr. W. J. Huff, of the Bureau of Mines) is to set the beaker on an electric hot plate with a glass triangle and watch glass over it (fig. 2). A glass tube lying on the hot plate encircles the beaker, rises, and projects down over the rim of the beaker for about 1 inch. A gentle stream of dried air freed from oxides of nitrogen is passed through the tube, keeping a small excess pressure on the inside of the beaker and so preventing contamination from the room air. The air, heated by passing through the section lying on the hot plate, materially assists evaporation. The solution is evaporated just to dryness (baking must be avoided), moistened with 2 c. c. of the 50–50 mixture of phenol-disulphonic acid and cold concentrated sulphuric acid, diluted with 10 c. c. of distilled water, and run through a filter paper into a Nessler tube, rinsing and washing as usual, then 15 c. c. of the 1 to 1 strong ammonia and water are added and the whole made up to 100 c. c. and compared with the standards. A blank is run with the sample.

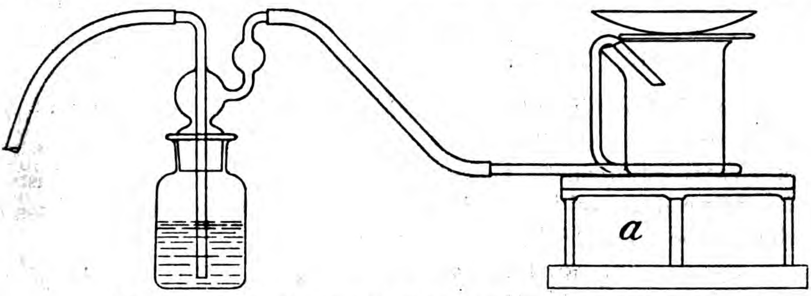

FIGURE 2.—Apparatus for evaporating solutions. *a*, Hot plate.

The amount of the sample taken is determined by filling the bottle with distilled water to the mark previously made when the bottle was removed from the bell jar and measuring the number of cubic centimeters of water used. The correct value in parts per million is obtained by calculation from the table of standards, which are based on 250 c. c. of gas.

The following table gives the analysis of mine air from the Miami mine of the Miami Copper Co., one-half mile west of Miami, Gila

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County, Ariz., where blasting is almost continuous. The samples were taken by Daniel Harrington, mining engineer, of the Federal Bureau of Mines, in cooperation with Koronski and McElroy, of the Public Health Service.

TABLE 2.—*Analysis of air from the Miami, Ariz., mine of Miami Copper Co.*

No. of sample.	Constituents.						Oxides of N_2.
	CO_2.	O_2.	CO.	CH_4.	N_2.	H_2.	
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Parts per million.*
11375	0.14	20.76	0.04	0.00	79.06	0.00	20
11376	.66	20.16	.03	.00	79.15	.00	15
11577	.19	20.62	.00	.00	79.10	.00	0
11578	.05	20.93	.00	.00	79.02	.00	0
11579	.17	20.79	.00	.00	79.04	.00	0
11550	.21	20.54	.05	.00	79.20	.00	60
11551	.27	20.48	.02	.00	79.23	.00	15
11552	.08	20.76	.00	.00	79.16	.00	0
11553	.21	20.69	.00	.00	79.16	.00	0

PHYSIOLOGICAL EFFECTS OF OXIDES OF NITROGEN.

The maximum percentages of oxides of nitrogen that may be present in mine air without harm to the workmen breathing it have not been clearly established. Gaseous products from the use of explosives not only produce oxides of nitrogen but such other harmful gases as carbon monoxide. Irvine[7] found that—

> In accidents due to the fumes of explosives, carbon monoxide accounts for most of the deaths, but nitrous fumes poisoning may also result and is the characteristic form of poisoning in accidents due to the inhalation of the fumes of burning nitroglycerin explosives.
>
> Partial burning or imperfect detonation causes CO and NO_2 gases. CO is produced in dangerous quantities after ordinary blasting but not NO_2.
>
> Nitrous fumes are intensely poisonous and of all gases the most treacherous. Haldane exposed mice to 0.05 per cent nitric oxide gas for 30 minutes and the mice were dead in 24 hours. The symptoms were the same whether nitric oxide or fumes of burning dynamite were used. Mann[8] found 0.026 per cent in mine air after blasting. Air containing enough NO_2 fumes to cause irritation in the nose or air passages is very dangerous.

Irvine[9] also states that—

> A certain number of cases returned as pneumonia amongst underground workers are really cases of nitrous fume poisoning, and the intensely irritating character of nitrous fumes has suggested that the repeated inhalation of small quantities of this gas may, by maintaining a catarrhal condition of the air passages and lungs, be a contributory factor in the development of "miners' phthisic."

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[7] Irvine, L. G., Accidents from poisonous asphyxiating gases in mines: Coll. Guard., vol. 111, 1916, pp. 653–655.

[8] Mann, E. A., Gassing: Dept. of Minister for Mines, Western Australia, Bull. 2, 1906, pp. 4, 7–9.

[9] Irvine, L. G., Accidents from poisonous asphyxiating gases in mines: Coll. Guard., vol. III, 1916, pp. 653–655.

Mann[10] says:

> CO and oxides of nitrogen occur together because they come from the same source. Almost all cases of gassing, therefore, are to some extent mixed poisoning. In practice, however, the symptoms of one or the other of these gases predominates sometimes to the exclusion of the appearance of poisoning of any other gas.

Lehmann and Hasegawa[11] found that 39 (0.0039 per cent) parts per million can be tolerated by many individuals for several hours.

Seventy-eight parts per million (0.0078 per cent of oxides of nitrogen) can be borne for only one-half hour.

One hundred seventeen to one hundred fifty-six parts per million (0.0117 to 0.0156 per cent) are directly dangerous.

Two hundred thirty-seven to three hundred ninety parts per million (0.0237 to 0.0394 per cent) increase danger rapidly.

Seven hundred eighty parts per million (0.078 per cent) kill animals quickly.

SYMPTOMS OF POISONING BY OXIDE OF NITROGEN FUMES.

Irvine says that in cases of poisoning by oxide of nitrogen fumes from explosives no symptoms may be evident and no poison or discomfort be felt for a time, yet within 12 to 18 hours after exposure the person exposed to the fumes may die from acute hemorrhagic oedema of the lungs.

Carbon monoxide may contribute to some extent to deaths from poisoning by oxides of nitrogen fumes. The affinity of oxygen for nitrogen oxide renders its physiological action difficult to study. The progress of the poisoning is, however, described by Oliver as follows:[12]

> During the inspiration of NO_2 there is a sensation of painful burning in the throat, which ceases when the fits of coughing have rejected the poison from the lungs. A few hours afterwards, when it would seem as if all symptoms had ceased and all fear of possible complications had passed away, the individual who has breathed the gas begins to complain of severe compression of the chest and of respiration being painful, he becomes pale, temperature elevated, the pulse frequent and small, and the patient succumbs without loss of his intellectual functions.

Dr. Black[13] says:

> The effects of the air passages, etc., are of an instant nature but the instant effect at the time is not so great that a man unaware of the real danger will al-

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[10] Mann, E. A., Gassing: Dept. of Minister for Mines, Western Australia, Bull. 2, 1906, pp. 4, 7–9.

[11] Lehmann, K. B., and Hasegawa, —, [Studies on the action of technically and hygienically important gases and vapors upon man. The nitrous gases: Nitric oxide, nitrogen peroxide, nitrous avid]: Archiv für Hygiene, Jahrg. 77, pp. 323–68.

[12] Oliver, Thomas, Diseases of occupation from legislative, social, and medical points of view: New York, 1908, p. 276.

[13] Black, E., Report of Royal Commission on Ventilation and Sanitation of Mines (Western Australia); Notes on the effects on men of noxious gases met with in and about mines, and on sundry matters affecting the health of miners: 1905, p. 79.

ways endeavor to escape at once. On the other hand the effects which may develop a few hours after exposure are most serious. Very actute bronchitis and oedema of the lungs may set in, ending rapidly in death. Habiltually breathed in small quantities and great dilution it produces severe chronic diseases. In acute poisoning immediate dyspnoea, tightness of chest, coughing, fainting, cyanosis, diarrhea, and collapse result. Death may occur in 40 hours, though symptoms of slight poisoning are delayed, in which case the first symptoms are headache, desire for fresh air, thirst, and then suddenly symptoms of an aggravated character, distress of breathing, anxiety depicted on the face, cold perspiration, protruding eyeballs, and spasmodic coughing followed by vomiting.

TREATMENT.

Persons should be removed from the vitiated atmosphere as soon as possible. In commencing oedema of the lungs administer atropin. When oedema is absent, inhalation of vapor of water and a little ammonia. In cyanosis, alkaline salt injection. The bronchitis, etc., are treated in the usual way. Dr. Seyfert's observations show that chloroform admin'stered internally in solution immediately after exposure to nitrous fumes and at short intervals thereafter is the most efficient mode of treatment in such cases. Full doses should be given every half hour.

The physiological effects found by different authorities are given here for the purpose of showing the necessity of a method of analysis for very low concentrations.

SUMMARY.

1. This paper describes a method for determining small quantities of oxides of nitrogen, other than N_2O. It has been developed from the usual procedure of water analysis.
2. With a 250-c. c. sample as low as 10 parts of oxides of nitrogen (other than N_2O) per million parts of air can be determined with an accuracy of about 5 parts per million.

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